

# Trends of CO at Hawaii: Seasonal Cycles and Decreasing Concentrations

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## INTRODUCTION

The importance of carbon monoxide in global change science comes from its role in affecting, or perhaps controlling, the concentrations of tropospheric OH radicals. Tropospheric OH is the main oxidant in the vast non-urban atmosphere. Increases of CO, for instance, may trigger a decrease in the oxidizing capacity of the earth's atmosphere that could indirectly lead to global warming and stratospheric ozone depletion. That this would happen was indeed the current thinking since the concentrations of CO were observed to be increasing [Khalil and Rasmussen, 1985; Levine *et al.*, 1985; see also Thompson and Cicerone, 1986]. Recent data, however, show that CO concentrations have now begun to decline, eliminating this potentially significant reinforcement of climatic change.

This paper will discuss the data taken in Hawaii at two sites: Cape Kumukahi and Mauna Loa Observatory (21.08°N, 157.1°W) and, specifically, to evaluate the trends and seasonal cycles of CO at these sites. Both sites are located on the island of Hawaii. Mauna Loa is at an altitude of 3.4 km and Cape Kumukahi is nearby at sea level. The existence of two sites, so close to each other, provides a unique data set on the cycles and trends of trace gases in and above the boundary layer in the northern hemisphere tropics [see Khalil and Rasmussen, 1981].

## SAMPLING AND ANALYSIS

Samples were collected in triplicate using a pump, in 0.8-L stainless-steel cans that are especially designed for the analysis of clean background air. The cans are internally passivated by a combination of processes that include eltopolishing. Each can is tested and certified before it is used in the field. Concentrations are stable for more than a year in these sampling containers [see Rasmussen and Khalil, 1980].

The samples were analyzed by a Carle 211 MS GC/FID and Trace Analytical HgO GC/RGD. Measurements before 1984 were by GC/FID and afterwards by both instruments. The detection limits are 5 ppbv (RGD) and 20 ppbv (FID). Triplicates usually agree within 1-2%. If one is more than about 20% different from the other two, it is eliminated (very few were discarded). The stability of the calibration standards is determined by periodic measurements. The records show no significant drifts [Khalil and Rasmussen, 1994].

## CONCENTRATIONS, SEASONAL CYCLES AND TRENDS

**Concentrations:** Table 1 contains the seasonally averaged CO concentrations at the two sites (also shown in Figure 1). The most prominent feature of the record is the seasonal cycle (about 50-110 ppbv). This cycle is caused by three processes which, in the order of their importance, are the seasonal changes in the removal of CO by reaction with OH, seasonal changes in the emissions, and variations in transport.

**Seasonal Cycles.** The seasonal cycle is the largest source of the variability of CO during the year. During the course of the experiment the average monthly concentration of CO is calculated as:  $\bar{C}_i = \sum C_{ij}/N$ . Here  $\bar{C}_i$  is the average concentration in month  $i$  (1...12) and  $C_{ij}$  is the average concentration in month  $i$  and year  $j$  (1,...,N). Since the trends are much smaller than the cycles, this calculation is an accurate representation of

TABLE 1. The Seasonal Average Concentrations of CO, and Their Variabilities at Mauna Loa Observatory and Cape Kumukahi, Hawaii

Month	CO Concentrations (ppbv)		Variability (ppbv)	
	Cape Kumukahi	MLO	Cape Kumukahi	MLO
Jan.	98.2 ± 5.8	84.0 ± 3.4	13.5	10.1
Feb.	98.4 ± 6.0	96.5 ± 4.7	18.7	16.9
March	105.7 ± 5.3	102.0 ± 2.7	10.6	17.2
April	107.4 ± 5.3	104.7 ± 1.9	10.7	12.2
May	94.2 ± 4.9	86.0 ± 3.5	10.6	12.1
June	78.7 ± 5.2	69.0 ± 1.3	8.4	8.0
July	60.0 ± 3.6	56.8 ± 2.0	6.3	7.3
Aug.	53.6 ± 6.0	48.8 ± 1.8	5.0	3.9
Sept.	61.2 ± 4.6	57.6 ± 1.6	6.2	7.0
Oct.	68.0 ± 6.1	60.5 ± 1.5	6.3	8.1
Nov.	73.6 ± 4.9	67.6 ± 1.9	8.0	14.3
Dec.	86.0 ± 5.4	76.2 ± 3.2	14.8	10.5

The  $\pm$  values are 90% confidence limits of the mean concentrations. The last two columns show the variability in each month. It is defined as the average (over 12 years of data) of the monthly standard deviations.

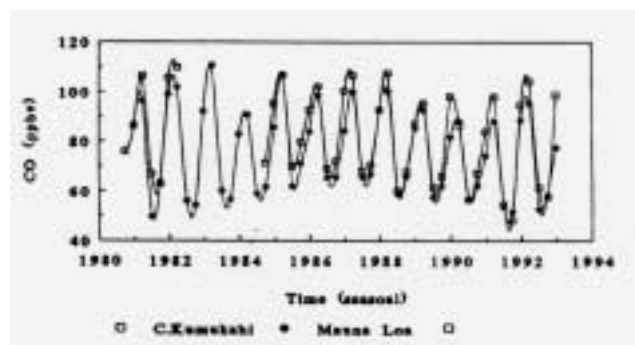


Fig. 1. Seasonally-averaged concentration of CO (ppbv) at Mauna Loa and Cape Kumukahi over a 12-year period. Concentrations at Cape Kumukahi are higher than at Mauna Loa at an average difference of 5 ppbv. The most significant variability is the seasonal cycle that is similar at the two sites.

the seasonal cycle (Table 2 and Figure 2a). In addition to the average cycle, the seasonal cycle of the variability can also be calculated as:  $\overline{Sd}_i = \sum S_{ij}/N$ , where  $S_{ij}$  is the standard deviation of the measurements in month  $i$  and year  $j$ . The results are shown in Figure 2b. The cycle of variability is highly correlated with the cycle of the concentration. In the winter, the concentrations of CO are the highest and so is the

TABLE 2. Seasonally-Averaged Concentrations of CO (ppbv) at MLO and Cape Kumukahi From 1980-1993

Time	Cape Kumukahi	MLO	Time	Cape Kumukahi	MLO
1980 Fall	76	-	1987 Winter	100	84
1981 Winter	86	87	Spring	107	100
Spring	106	97	Summer	68	66
Summer	67	50	Fall	71	67
Fall	63	64	1988 Winter	93	93
1982 Winter	106	99	Spring	108	100
Spring	110	102	Summer	60	59
Summer	-	56	Fall	68	66
Fall	-	54	1989 Winter	87	86
1983 Winter	-	92	Spring	96	93
Spring	-	111	Summer	62	58
Summer	-	60	Fall	66	62
Fall	-	57	1990 Winter	98	82
1984 Winter	-	83	Spring	86	88
Spring	-	91	Summer	57	57
Summer	-	59	Fall	67	62
Fall	71	62	1991 Winter	84	74
1985 Winter	95	86	Spring	98	88
Spring	107	107	Summer	55	54
Summer	70	62	Fall	48	52
Fall	80	71	1992 Winter	95	89
1986 Winter	93	84	Spring	104	96
Spring	102	99	Summer	62	53
Summer	69	66	Fall	58	59
Fall	72	66	1993 Winter	99	78

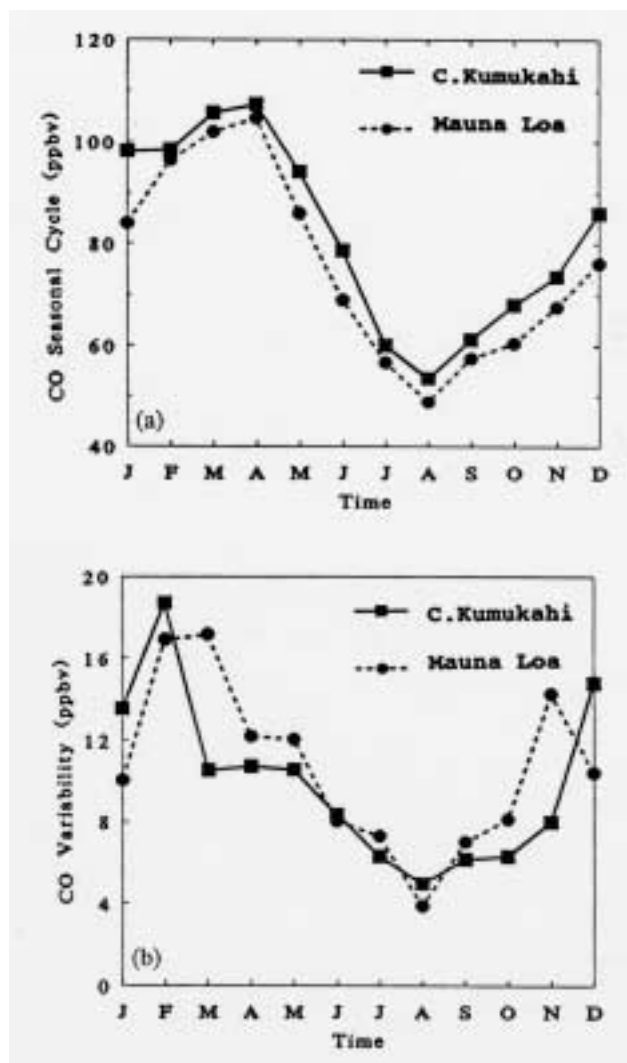


Fig. 2 (a). The average seasonal concentration of CO at Cape Kumukahi and Mauna Loa. The concentration at Cape Kumukahi (in the boundary layer) is higher than at Mauna Loa (above the boundary layer). The difference is about the same throughout the year. This feature is also observed for other trace gases. (b). The seasonal cycle of the variability of CO. The variability is defined as the average standard deviation of the monthly concentrations over the 12-year period of the record. The variability follows a pattern similar to the concentration. When the concentration is low the variability is low.

monthly variability. In the summer, the average concentrations and variability are the lowest.

*Trends:* In Figure 3, the 3-year running averages of the monthly concentrations of CO are plotted. By filtering the data over this period, most of the effect of the seasonal variations of CO (Figure 1) and other random variability are eliminated. The running

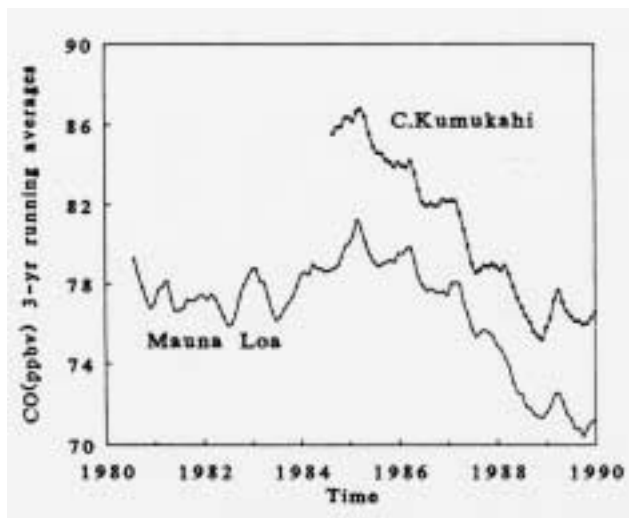


Fig. 3. Three-year running averages of CO concentrations (ppbv) based on monthly average concentrations. These calculations show the long term trends in which the effects of seasonal cycles are eliminated. The graphs show that CO may have been increasing in the beginning of the record and has been declining during the last 6 years or so at fairly rapid rates.

averages are plotted in the middle of the time over which the average is taken. This figure suggests that CO was increasing between 1980-1985 and has decreased since then. Similar trends were observed at other sites around the world. The earlier global increases in CO and the recent decreases are reported by *Khalil and Rasmussen* [1984, 1988, 1994] and by *Novelli et al.* [1994].

By looking at the seasonal minima in Figure 1, it is apparent that the concentration of CO increased in the early part of the record and has been decreasing in recent times. The trends are estimated quantitatively as follows: First, annual averages of the seasonally averaged data were taken. The annual averages are not affected by the seasonal variation (on the average). Then, the trends were calculated as:

$$\text{Trend } (i + \delta / 2) = \left( [C(i + \delta) - C(i)] / [\bar{C}(i)\delta] \right) \times 100\%$$

where Trend (i) is the rate of change of concentration at time  $i + \delta/2$ ,  $C(i + \delta)$  is the annual average concentration at time  $i + \delta$ ,  $C(i)$  is the annual concentration at time  $i$ ,  $\bar{C}(i)$  is the average concentration for the years between  $i$  and  $i + \delta$ .  $\delta$  is taken to be 5 years for the calculation discussed here. These calculations are shown in Figure 4. The results show that CO was increasing at about  $1\% \text{ yr}^{-1}$  in the early 1980s and has been decreasing in recent years at rates of  $-3\% \text{ yr}^{-1}$  or so. Similar declining trends are observed at other sites around the world [*Khalil and Rasmussen*, 1994; *Novelli et al.*, 1994].

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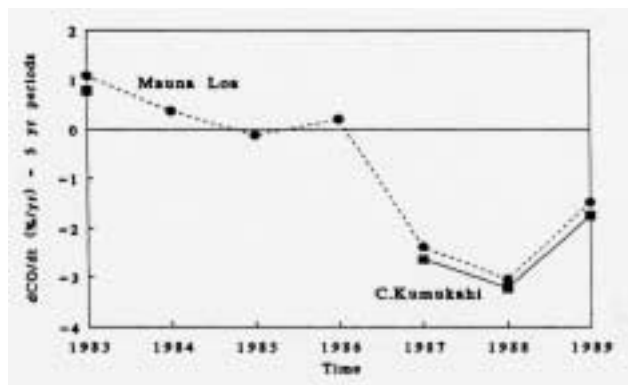


Fig. 4. The trends of CO. The trends are based on the annual averages of CO concentrations (see text). CO increased in the early part of the record and has declined in the recent 5 years. Both sites give the same results (note the trend at 1983 for Cape Kumukahi - for 1984-1986 there are no data to calculate the trends at this site).

## CONCLUSIONS

Measurements of CO showed that between the 1950s and middle 1980s, the concentrations of CO were increasing. This increase may have gone on for longer times [*Khalil and Rasmussen*, 1988; *Rinsland et al.*, 1985]. Since then, however, the concentrations appear to be declining. Both of these observations are in accord with our understanding of the sources and sinks of CO. Anthropogenic emissions have been increasing over the last 50 years. Major anthropogenic sources include urban areas (with many sources such as automobiles) and biomass burning [see *Logan et al.*, 1981; *WMO*, 1986, 1991; *USEPA*, 1990]. Emissions of other hydrocarbons (including methane) may also have contributed to increasing trends. In recent years, however, the urban sources of CO in the United States and in Europe, have decreased rapidly because of air quality regulations. The decrease of CO in the southern hemisphere is most easily explained by a hypothesized decrease or a stabilization in tropical biomass burning. Whether biomass burning is decreasing awaits direct observational and statistical verification. In addition to the decreasing emissions, there are various possibilities that may have caused an increase of OH at some latitudes that would also lead to a decrease in CO [see *Madronich and Granier*, 1992]. All of these processes would lead to declining global concentrations of CO since it has a relatively short lifetime and responds quickly to changes in emissions or sinks. Yet at this time, it is impossible to say whether these declining trends will continue. It is clear, however, that the current declining trend shows an improvement in global air quality.

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## REFERENCES

- Khalil, M.A.K., and R.A. Rasmussen, Differences in the concentrations of trace gases in and above the tropical boundary layer, *Pure Appl. Geophys.*, *119*, 990-997, 1981.
- Khalil, M.A.K., and R.A. Rasmussen, Carbon monoxide in the Earth's atmosphere: Increasing trend, *Science*, *224*, 54-56, 1984.
- Khalil, M.A.K., and R.A. Rasmussen, Causes of increasing atmospheric methane: Depletion of hydroxyl radicals and the rise of emissions, *Atmos. Environ.* *19*, 397-407, 1985.
- Khalil, M.A.K., and R.A. Rasmussen, Carbon monoxide in the earth's atmosphere: Indications of a global increase, *Nature*, *332*, 242-245, 1988.
- Khalil, M.A.K., and R.A. Rasmussen, Global decrease of atmospheric carbon monoxide, *Nature*, *370*, 639-641, 1994.
- Levine, J.S., C.P. Rinsland and G.M. Tenille, The photochemistry of methane and carbon monoxide in the troposphere 1950 and 1985, *Nature*, *318*, 254-257, 1985.
- Logan, J.A., M.J. Prather, S.C., Wofsy, and M.B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res.* *86*, 7210-7254, 1981.
- Madronich, S., and C. Granier, Impact of recent total ozone changes on tropospheric ozone photodissociation, hydroxyl radicals and methane trends, *Geophys. Res. Lett.* *19*, 465-467, 1992.
- Novelli, P.C., K.A. Masarie, P.P. Tans, and P.M. Lang, Recent changes in atmospheric carbon monoxide, *Science*, *263*, 1587-1590, 1994.
- Pinto, J.P., and M.A.K. Khalil, The stability of tropospheric OH during ice ages, inter-glacial epochs and modern times, *Tellus*, *43B*, 347-352, 1991.
- Rasmussen, R.A., and M.A.K. Khalil, Atmospheric methane (CH<sub>4</sub>): Trends and seasonal cycles, *J. Geophys. Res.*, *86*, 9826-9832, 1981.
- Rasmussen, R. A., and M.A.K. Khalil, Atmospheric methane (CH<sub>4</sub>): Trends and seasonal cycles, *Proceedings, NATO Advanced Study Institute on Atmospheric Ozone*, edited by A.E. Aikin, Dept. Trans., Washington, DC., 1980.
- Rinsland, C.P. and J.S. Levine, Free tropospheric carbon monoxide in 1950 and 1951 deduced from infrared total column amount measurements, *Nature*, *318*, 250-254, 1985.
- Thompson, A.M. and R.J. Cicerone, Possible perturbations of CO, CH<sub>4</sub> and OH, *J. Geophys. Res.* *91*, 10,853-10,864, 1986.
- USEPA (U.S. Environmental Protection Agency) Air Quality Criteria for Carbon Monoxide, EPA, 551 pp., Washington, D.C., 1990.
- WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion: 1991*, 211 pp., WMO, Geneva, 1991.
- WMO (World Meteorological Organization), *Atmospheric Ozone 1985*, 1094 pp., WMO, Geneva, 1986).